

PATENT SPECIFICATION

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(S4) PURIFICATION OF BRINE

(71) We, CANADIAN INDUSTRIES LIMITED, a corporation of Canada, of 630 Dorchester Blvd. West, Montreal, Quebec H3C 2R3, Canada, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:

10 This invention relates to a process for the purification of brines suitable for use in the manufacture of chlorine and caustic alkali by electrolysis, and more specifically to a process for the removal of soluble sulphates from said brines.

15 Chlorine and caustic alkali are produced by the electrolysis of alkali metal chloride-containing brines employing mercury or diaphragm cells. Efficient operation of the electrolysis process requires that brines employed contain only minor amounts of dissolved sulphates. It is known to precipitate the sulphate from said brines as barium sulphate but this procedure requires the use of relatively costly barium compounds. It is also known to precipitate the sulphate of brines as calcium sulphate using calcium chloride as the precipitant. However, this latter procedure suffers from the disadvantage that calcium sulphate is more soluble than barium sulphate and as a result it is difficult to reduce the sulphate to the desired low level. In the article "Brine Purification for the Mercury Cell Process" by Kinji Harada and Katsuji Yamori published in Electrochemical Technology, volume 5, No. 3-4, pages 137 to 143, 1967 it is indicated in Figure 8 that precipitation of sulphate from brines employing calcium chloride as precipitant will result in a reduction of sulphate (SO₄) during the desulphation step from 7.0 grams per liter to 3.8 grams per liter. However, it is preferred to reduce the sulphate in the brine to a value in the range 2 to 5 grams per liter Na₂SO₄ (1.35 to 3.4 grams per liter SO₄).

It has now been found that the sulphate content of an alkali chloride-containing brine can be reduced to as low as 2 grams per

liter of SO₄ by the addition of a stoichiometric excess of calcium chloride while maintaining the pH of the brine in the range 7 to 9 and the temperature in the range 30°C to 50°C. The calcium sulphate precipitate formed under these conditions settles rapidly to a compacted sludge permitting easy separation of the sulphate as sludge.

Accordingly this invention provides a process for the removal of soluble sulphate from brines suitable for use in the manufacture of chlorine and caustic alkali by electrolysis which comprises (1) mixing with a brine containing sodium chloride or potassium chloride maintained at a pH in the range 7 to 9 and at a temperature in the range 30°C to 50°C a stoichiometric excess of calcium chloride, thus forming insoluble calcium sulphate, and (2) separating the calcium sulphate from the brine.

The maintenance of a pH in the range 7 to 9 is necessary in order to obtain a rapid settling rate and low volume of the calcium sulphate sludge.

The brines to which the process of this invention are applicable are those containing major amounts of sodium chloride or potassium chloride. Usually such a brine will contain from 10% to 25% by weight of sodium chloride or potassium chloride. When the brine originates from the caustic evaporation stage of a diaphragm cell process it will contain about 25% alkali metal chloride, about 4% alkali metal sulphate and about 0.5% alkali metal hydroxide. This latter brine which is alkaline is hereinafter called "sulphate purge". The calcium chloride reagent is preferably used in the form of an aqueous solution, containing from 12 to 27% by weight of calcium chloride.

Preferably the removal of sulphate from brines is carried out in concentrated systems. Normally the brine will be concentrated, and it is preferred to use as precipitant a concentrated aqueous solution of calcium chloride. A concentrated system is also of advantage because this will minimize the amount of water that must be removed during the chlor-alkali process.

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The pH of the brine is adjusted by the addition of an acid. Preferably hydrochloric acid is employed. If sulphuric acid is employed for this purpose it will result in a slight increase in the calcium sulphate precipitate.

As an aid to the formation of a calcium sulphate precipitate it is of advantage to add to the brine, prior to addition of calcium chloride, a portion of calcium sulphate, preferably a portion of a calcium sulphate sludge from a previous precipitation.

The pH adjustment and calcium chloride addition is conveniently carried out in a stirred reactor equipped with a pH controller. A five minute residence time in the reactor is normally sufficient. The calcium sulphate slurry from the reactor is then transferred to a settling vessel or pond.

The process of this invention provides a means for reducing the sulphate content of a chlor-alkali plant brine feed to an acceptable low level by the use of a calcium salt as precipitant.

The invention is illustrated additionally by the following Examples but its scope is not limited to the embodiments shown therein. Unless otherwise stated percentages are by weight.

EXAMPLE 1

To a brine containing 24.2% sodium chloride, 4.4% sodium sulphate and 0.6% sodium hydroxide was added 1.14 times the stoichiometric amount of calcium chloride in aqueous solution while maintaining the mixture at a pH of 9 by addition of hydrochloric acid. The temperature of the mixture was 38°C. The mixture was stirred for 1 minute and allowed to settle. Analysis of the supernatant liquid showed that the sulphate (SO₄) content had been reduced

to 2 grams per liter from the initial value of 29.6 grams per liter.

EXAMPLE 2

Employing the brine of Example 1 the effect of pH on the rate of settling and volume of the calcium sulphate precipitated was investigated. The brine before treatment had a pH of 12.3. When calcium chloride solution alone was employed the resulting slurry had a pH of 11.7. The temperature of the slurry was 38°C. The precipitate was bulky, amounting to 40% of the original volume of the slurry after settling for 24 hours. When the pH of the slurry was reduced to 9 by addition of hydrochloric acid the settled sludge occupied only 16% of the original volume of the slurry after 1 hour. Further decrease in pH caused only a slight reduction in sludge volume.

The order in which pH adjustment and calcium chloride addition took place did not appear to be critical. However, simultaneous pH adjustment and calcium chloride addition caused a somewhat greater reduction in sludge volume than when these were done sequentially.

EXAMPLE 3

To a 2 liter brine sample containing 24.6% sodium chloride, 5.6 grams per liter sodium hydroxide, 29.6 grams per liter SO₄⁻ and 8.8 ppm Ca⁺⁺ were added 100 mls of calcium sulphate sludge from a previous run. The brine was maintained at 38°C and 812 grams of a calcium chloride solution containing 12% calcium chloride were added while adjusting the pH from 12.3 to 9 with hydrochloric acid. After 1 minute of mixing with a stirrer operating at 150 rpm the mixture with a total volume of 2160 mls was allowed to settle. The following results were obtained.

Settling Time minutes	Suspended Solids in Supernatant Liquid ppm	Analysis of Supernatant Liquid	
		SO ₄ ⁻ g/l	Ca ⁺⁺ ppm
15	99	1.58	2420
30	3	1.49	2420
45	0	1.59	2420
60	0	1.60	2340

The volume of the settled sludge was 350 mls equivalent to 16% of the original slurry volume and contained 17% solids. The sludge was filtered and dried. The dry sludge cake was found to contain approximately 80% calcium sulphate and 1% water. Sulphate removal was 95%. The sodium chloride content of the dry sludge cake was 11% when the sludge was not washed with water before drying, and 5% when washed.

24.2% sodium chloride, 4.4% sodium sulphate and 0.6% sodium hydroxide and having a pH of 11.7 were added 350 grams of 27% calcium chloride solution. The mixture was agitated for 15 minutes and allowed to settle. The temperature of the mixture was 38°C. After 24 hours the volume of settled sludge was 900 mls and amounted to 40% of the original volume of the slurry (2250 mls). Sulphate removal was 78%.

EXAMPLE 4

To 2 liters of a sulphate purge containing

EXAMPLE 5

The procedure of Example 4 was repeated

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except that the pH of the purge was adjusted to a value of 8 before adding the calcium chloride solution. The temperature of the mixture was 38°C. After settling for 1 hour the volume of the settled sludge (370 mls) amounted to 16% of the original volume of the slurry (2250 mls). Sulphate removal was 93%.

EXAMPLE 6

This Example provides a comparison between the use of dilute calcium chloride solution as precipitant at the normal pH of the brine, and the use of concentrated calcium chloride at controlled pH. To 1 liter of sulphate purge containing 24.2% sodium chloride, 4.4% sodium sulphate and 0.6% sodium hydroxide was added 1 liter of 7% calcium chloride. There was no adjustment of pH, the pH of the mixture being approximately 12. The temperature was 36°C, the mixing time 5 seconds. The precipitate was allowed to settle and the volume of the sludge at times up to 60 minutes was measured. The following results were obtained.

Time minutes	Volume of Sludge ml.
0	2,000
5	1,000
8	880
30	820
60	810

Analysis of the supernatant liquid showed the presence of 2.5 g/l of sulphate (SO_4), corresponding to 5 g/l sulphate remaining in the sulphate purge.

To 1 liter of the same sulphate purge were added 175 grams of 27% aqueous calcium chloride solution, the pH being adjusted with hydrochloric acid to a value of 9. The temperature was 36°C, the mixing time 15 minutes. The precipitate was allowed to settle and the volume of sludge measured as above. The results were as follows.

Time minutes	Volume of Sludge ml.
0	1,190
5	819
8	580
15	300
60	290

Analysis of the supernatant liquid showed the presence of 2.5 g/l of sulphate (SO_4), corresponding to 2.9 g/l sulphate remaining in the sulphate purge. The second treatment thus was twice as efficient as the first. The settled sludge volume of the second treatment was only 36% of that of the first one after 60 minutes settling.

EXAMPLE 7

The settling rate of calcium sulphate precipitated from a brine containing sodium sulphate was measured employing a settling column 8 feet high and 1 foot in diameter. 281 pounds of brine containing 23.9% by weight of sodium chloride, 4.4% by weight of sodium sulphate and 0.6% by weight of sodium hydroxide were placed in the settling column and 181 pounds of 12.2% by weight aqueous calcium chloride solution were added at 40°C. with sufficient hydrochloric acid being added to bring the pH of the mixture to 9. The mixture contained 20.3% by weight of sodium chloride. After mixing, the calcium sulphate precipitate formed was allowed to settle. Samples of the mixture in the column were taken periodically at 1 foot height intervals over a period of 3 hours. The percentage solids was determined for each sample. Then for each sampling point percentage solids was plotted against time to obtain the time for 70% solids removal, t_{70} , at that height. The results were as follows:—

Height feet	t_{70} minutes
0 bottom	
1	
2 1/2	142
3 1/2	100
4 1/2	100
5 1/2	86
6 1/2	60
7 1/2	50

From a graphical plot of height versus t_{70} the slope of the curve, the settling rate, was found to be 2.8 feet per hour.

WHAT WE CLAIM IS:—

1. A process for the separation of sulphates from brines suitable for use in the manufacture of chlorine and caustic alkali by electrolysis, comprising the steps of

- (1) maintaining a brine containing sodium chloride or potassium chloride at a pH of 7 to 9 and a temperature of 30°C to 50°C,
- (2) mixing said brine with a stoichiometric excess of calcium chloride, thus forming insoluble calcium sulphate, and
- (3) separating the calcium sulphate from the brine.

2. A process as claimed in Claim 1 wherein the brine contains from 10% to 25% by weight of sodium chloride or potassium chloride.

3. A process as claimed in Claim 1 or 2 wherein the calcium chloride reagent is an aqueous solution of calcium chloride containing from 12% to 27% by weight of calcium chloride.

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4. A process as claimed in Claim 1, 2 or 3 wherein a portion of calcium sulphate is added to the brine prior to the addition of calcium chloride.

cipitation is added to the brine prior to the addition of calcium chloride.

5. A process as claimed in any one of claims 1 to 4 in which the pH is adjusted by the addition of an acid.

8. A process as claimed in claim 1 substantially as hereinbefore described with reference to any one of Examples 1 to 3 or 5 to 7.

6. A process as claimed in claim 5 in which the acid is hydrochloric or sulphuric acid.

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7. A process as claimed in any one of claims 1 to 6 in which a portion of a calcium sulphate sludge from a previous pre-

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